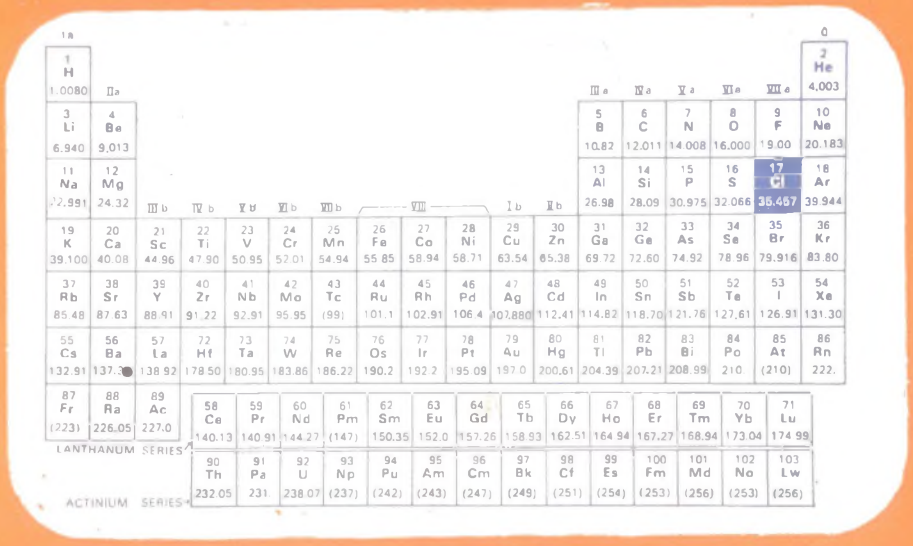
THE STORY OF THE ELEMENTS

Chlorine

(Part I)



Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1 H 1.0080																	2 He 4.003
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32											13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.92	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.3	57 La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 208.99	84 Po 210	85 At (210)	86 Rn 222.
87 Fr (223)	88 Ra 226.05	89 Ac 227.0															

LANTHANUM SERIES

58 Ce 140.13	59 Pr 140.91	60 Nd 144.27	61 Pm (147)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
90 Th 232.05	91 Pa 231	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (256)

ACTINIUM SERIES

September—October 1978

SARABHAI M CHEMICALS

THE STORY OF THE ELEMENTS

Chlorine

(Part One)

SARABHAI M CHEMICALS
BARODA

HISTORIC MILESTONES

1648 JOHANN RUDOLPH GLAUBER, a German Chemist described the preparation of hydrogen chloride from common salt and oil of vitriol.

1742 JOSEPH PRIESTLEY collected the hydrogen chloride gas over mercury and determined its properties.

1774 CARL WILHELM SCHEELE described the preparation of *"dephlogisticated marine acid air"* which obtained during his researches on the properties of black oxide of manganese.

1785 COUNT CLAUDE-LOUIS BERTHOLEET observed and put in practice the bleaching properties of gas and its solution in water.

1787 ANTOINE - LAURENT LAVOISIER coined the name *"acide muriatique"* from which English name Muriatic acid is derived.

1789 BERTHOLLET made convenient alkaline bleaching solution.

1799 CHARLES TENNANT of Glasgow patented the method of preparing *"bleaching powder"* by absorbing chlorine in dry hydrated lime.

1800 LAVOISIER and BERTHOLLET preferred the name *"Oxymuriatic acid"* for SCHEELE's product.

1805 SIR HUMPHRY DAVY first liquefied the gas prepared by SCHEELE.

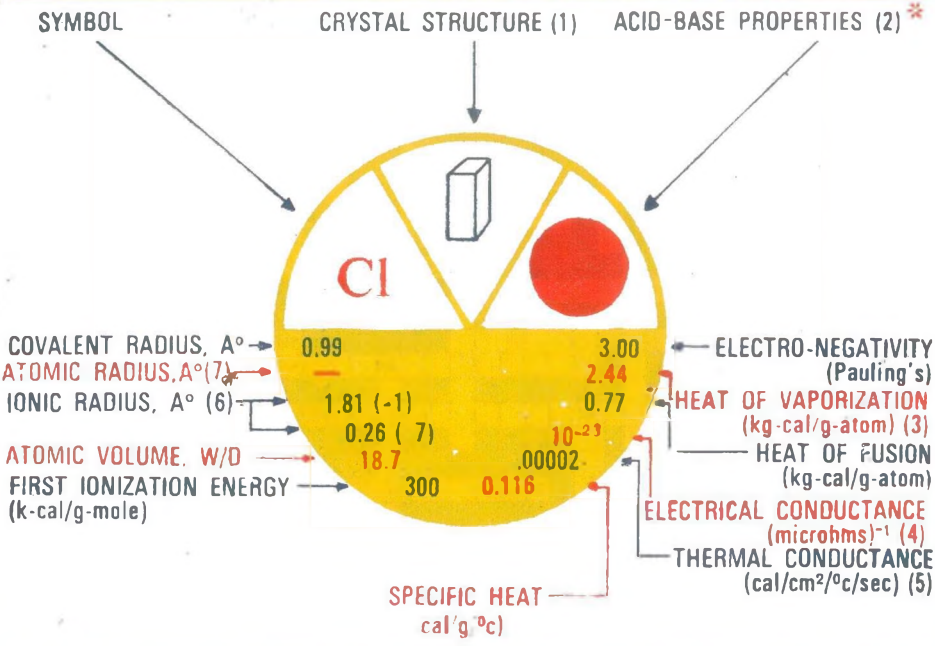
1809 LOUIS - JOSEPH GAY - LUSSAC and LOUIS JACQUES THENARD suggested that *"Oxymuriatic acid"* was an element.

1810 DAVY adduced evidence that the gas was an element, and named it chlorine from the Greek word Chloros meaning *'greenish yellow'* -- the colour of the gas.

1851 CHARLES WATT, in Great Britain, patented first electrolytic process for manufacturing chlorine.

1868 HENRY DEACON produced chlorine from hydrochloric acid and oxygen using copper chloride absorbed in pumice stones as a catalyst.

PERIODIC PROPERTIES OF CHLORINE



*

Strong

Medium

Weak

(1) Tetragonal

(2) Oxides of Chlorine are acidic in character, and are indicated by dark red colour. Intensity of colour indicates relative strength.

(3) At boiling point.

(4) From 0° C to 20°C.

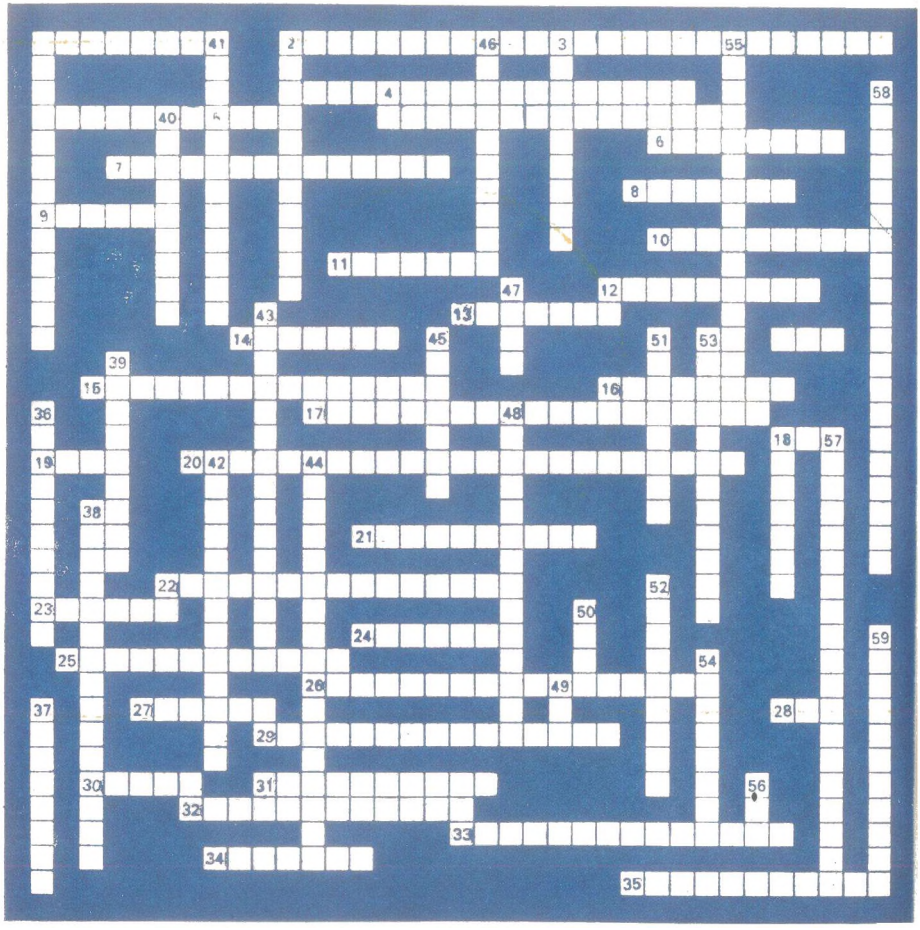
(5) At room temperature.

(6) Ionic (crystal) radii for co-ordination number 6.

(7) Metallic radii for co-ordination number of 12.

Sarabhai M Chemicals.

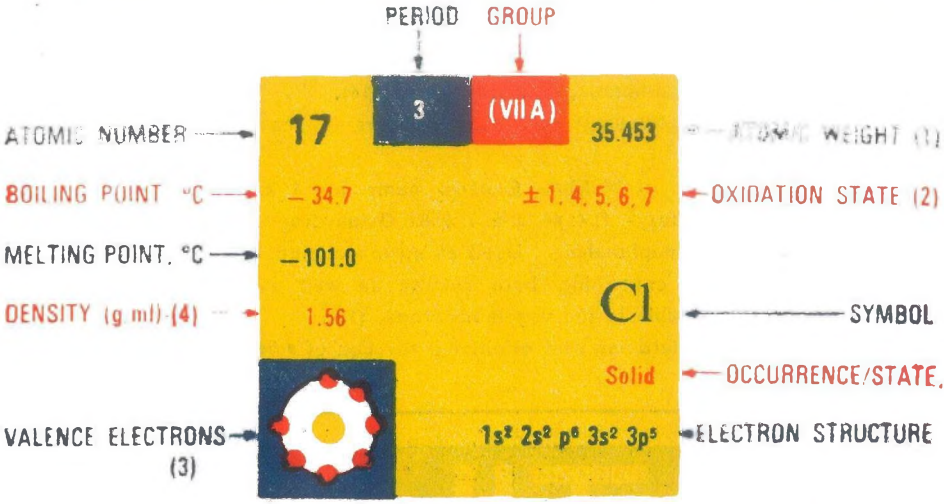
Chemistry Cross-Word Puzzle (Chlorine)



HORIZONTAL LEGEND

1. A pungent-smelling, greenish-yellow gas belonging to the Halogen Family. Known for its bleaching characteristics. (8).
2. *"Chlorine"* was named from the *Greek word* meaning *yellow-green*. Name this Greek Word. (7).
3. Colour of the chlorine gas. (8 + 6).
4. An antimicrobial drug containing chlorine, which is best known after its Trade Name rather than its generic name. (13).

PHYSICAL PROPERTIES OF CHLORINE



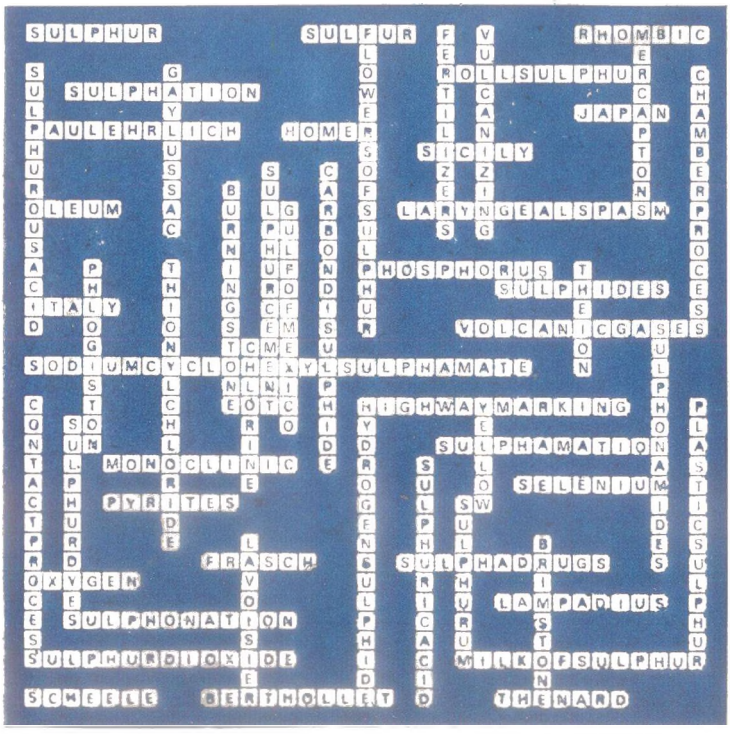
(1) Based upon Carbon-12.

(2) The element Chlorine has Five, Oxidation states ± 1, 4, 5, 6, 7 of which ± 6 is most stable.

(3) Chlorine has 6 valence electrons in its outermost orbit.

5. A sweet smelling organic solvent, which is also used as an *inhalation anesthetic*. (10).
6. A vertical neighbour of chlorine and the first member of the *Halogen Family*. (8).
7. An oily liquid, having an amine odour, used as a *tranquilizer, sedative* and *antiemetic*. It is used in the treatment of anxiety, tesion, agitation, schizophrenia, acule alcoholism, status asthmaticus, nausea, vomiting, tachycordia, hypothermia, dermatitics, etc. (14).
8. A *horizontal* neighbour of chlorine. It occurs in the volcanic countries. (7).
9. A stereoisomer of *dieldrin*. Generic name for 1: 2: 3: 4: 10: 10-hexachloro-6: 7:- epoxy- 1: 4: 4a: 5: 6: 7: 8: 8a-Octahydro 1: 4-endo endo 5: 8-dimethano naphthalene Used as an insecticide. (6).
10. An insecticide containing both *chlorine* as well as *sulphur*. It is specially applicable to the vegetable crops. (10).
11. A scottish obstetrician who originated the use of *ether* as anaesthetic

Continued on Page 23



Solution to the Chemistry Cross Word Puzzle SULPHUR published in "The Story of the Elements". SULPHUR (Part One

CHLORINE

PART ONE

CHLORINE, A CHEMICAL ELEMENT OF the Halogen Family, is a strong smelling, greenish-yellow gas. Element number 17, Chlorine, Cl, is second in reactivity only to fluorine among the halogen elements, and hence, is never found free in nature, except at the elevated temperatures of volcanic gases. However, it occurs most abundantly in soluble chlorides. It is estimated that 0.045% of the earth's crust is chlorine, and thus it becomes the twelfth most common element of the earth's crust.

Chlorine was probably known to the alchemists of the 13th century, but SCHEELE was the first to describe its preparation (1774). It received its present name from DAVY (1810).

It causes severe suffocation, constriction in the chest, tightness in the throat and edema of the lungs after severe exposure. Chlorine as chloride is an essential constituent of animal life.

Chlorine is an excellent oxidizing agent. Historically, the use of chlorine as a bleaching agent in the paper, pulp and textile industries, and as a germicide for drinking water preparation, swimming pool purification, and hospital sanitation has made community living possible.

Chlorine reacts with various compounds or metals to form respective inorganic or Organic chloro–compounds, such as : hydro - chloric acid, sodium chloride, bleaching powder, hypochlorite solutions, aluminium chloride, chloroform, carbon tetrachloride, chlorat, DDT, Vinyl chloride, chlorobenzene, and so on.

Chlorine as such, or in the form of one of its several active combinations, now is used principally in the manutacture of metallic chlorides, hypochlorites, bromine, ethylene glycol, tetraethyllead, lubrication aids, solubilizing starch, and many intermediates used for the preparation of dyes, synthetic drugs and plastics. Chlorine is used in the pulp and paper industry for bleaching wood pulp, waste paper, and other paper-making fibers as well as for control of slime. Chlorine and its active derivatives are used to control bacterial, algae molds, and other microplant and animal life in municipal and industrial waters, sewage, and other wastes. Other important uses include disinfection of swimming pools and bathing beaches; sterilization of utensils and containers in dairies, breweries. carbonated beverage plants, public food and beverage dispensers, and packing and poultry houses; controlling odours in rendering and fertilizer plants; and the bleaching of cotton, linen, rayon, rags, shellac, flour and other materials.

DISCOVERY

THE DISCOVERY OF CHLORINE HAS ALWAYS BEEN CAPTIVATING like that of other elements of the periodic system. The story of the discovery of chlorine would remain incomplete without reviewing the discovery of the Halogens—namely. Fluorine, Chlorine, Bromine, Iodine and Astatine. Chlorine is the second member of the *Halogen Family.*

DISCOVERY OF HALOGENS

The discovery of the four halogens required a little more than a century. Although SCHEELE prepared chlorine in 1774 by the action of manganese dioxide on hydrochloric acid, it was believed to be compound until after 1810, when SIR HUMPHRY DAVY gave convincing proof of its elementary nature. In 1811. BERNARD COURTOIS isolated iodine from the mother liquor obtained by leaching the ashes of marine algae. BALARD's discovery of bromine fifteen years later was an especially important event in the history of science, for chemists were just beginning to realize that there are family groups among the elements and DOBEREINER soon observed that chlorine, bromine and iodine form a closely related triad. The long dangerous search for fluorine which brought suffering and death to several promising chemists, culminated successfully in 1886 through the brilliant efforts of MOISSAN. Search for the *missing halogen,* eka-iodine, was actively pursued for many years. CORSON, MACKENZIE and SEGRE' obtained the element number 85 by the use of the cyclotron, in 1945 and named it Astatine, in 1947.

DISCOVERY OF CHLORINE

In his famous research on pyrolusite, C. W. SCHEELE allowed hydrochloric acid, or Spiritus salis as he called it, to stand in contact with finely ground pyrolusite (crude manganese dioxide), and noticed that the acid acquired thereby a suffocating odour like that of warm aqua regia, and *"most Oppressive to the Lungs"*. He thought that the manganese dioxide had taken the combustible principle, *phlogiston,* from the hydrochloric acid, and therefore called the gas *"dephlogisticated marine acid"*, or *"dephlogisticated muriatic acid"*. He noticed that it dissolved slightly in water, imparting to it an acid taste, that it bleached coloured flowers and green leaves, and that it attacked all metals.

A. L. LAVOISIER thought that all acids contain oxygen. DR. WILLIAM HENRY, who obtained hydrogen by passing an electric discharge through gaseous *"marine acid"*, concluded that it came from water, and that water *must* be an essential constituent of hydrochlorid acid. C. L. BERTHOLLET, who was a partisan of LAVOISIER and not to a phlogistonist, noticed that calcined pyrolusite, which had lost some of the oxygen from its manganese dioxide yielded less of the suffocating gas, *"dephlogisticated marine acid"*, than could be obtained from an equal weight of fresh pyrolusite.

M.DE FOURCROY made use of the theory promulgated by M. LAVOISIER in his treatise : *"Elements of Chemistry and Natural History"* to explain the properties of dephlogisticated marine acid such as they were then known.

BERTHOLLET presumed that the gas now known as *chlorine* was a loose compound of hydrochloric acid and oxygen. In the year 1807. SIR HUMPHRY DAVY obtained hydrogen by the action of potassium on "muriatic acid", and concluded that it must have come from the water in the acid, and that the oxygen in the water must have converted the potassium to potassium oxide. GAY-LUSSAC and THENARD, however, did not accept the explanation. They argued that the hydrogen came neither from the acid nor from the water, but from the potassium, which was thereupon changed back into caustic potash, which then reacted with the acid. They tested the *Oxydized marine acid (chlorine)* with glowing charcoal, but since they could detect no oxygen they concluded that oxygen was formed only in the presence of water. All their attempts to decompose the chlorine by heating it with dry charcoal proved fruitless.

L. J. GAY-LUSSAC and L. J. THENARD believed (1) that muriatic gas contain one-fourth of its weight of water, (2) that Oxymuriatic gas is a compound of oxygen and *some other substance,* and (3) that the substance obtained by heating calomel with phosphorus is a triple compound consisting of dry muriatic acid, oxygen and phosphorus.

DAVY's final views on these three points were as follows : (1) muriatic acid is composed of oxymuriatic acid *(chlorine)* and hydrogen, (2) chlorine can not be dicomposed, and the substance obtained by heating calomel with phosphorus is a compound of chlorine and phosphorus.

DAVY usually attempted to avoid theorizing, and therefore claimed only to have shown that the properties of chlorine were most easily explained by assuming it was simple. He chose the name *chlorine,* Greek for *greenish yellow,* since this name did not commit him to any theory and could easily be changed if later discoveries required it.

Since BERTHOLLET, GAY-LUSSAC, THENARD, DE FOURCROY, and CHAPTAL all belonged to the French school founded by the illustrious LAVOISIER, it was difficult for them to admit the existence of an acid

that contained no oxygen, but nevertheless they soon had to yield to the convincing evidence presented by SIR HUMPHRY. DR. JOHN MURRAY in Edinburgh and BERZELIUS in Stockholm continued, however, for some time to regard chlorine as a compound.

After *iodine* was discovered in 1811, the evidence for the elementary nature of chlorine became still, more convincing, and by 1820 even BERZELIUS had yielded. When ANNA, his cook remarked one day that the flask she was washing smelled of *"Oxidized muriatic acid"*, BERZELIUS replied : "Anna, you *mustn't speak* of oxidized muriatic acid *any more;* from now on you must say *chlorine.*

The discovery of *bromine* by A. J. BALARD and the preparation of prussic (hydrocyanic) acid, an oxygen-free acid, by GAY-LUSSAC made the evidence conclusive. DAVY's formal announcement of the elementary nature of chlorine was made in memoir which he read before the Royal Society on November 15, 1810.

SIR HUMPHRY DAVY's life was a short one, and his last years were marred by continued illness. In a letter written in Rome in February, 1829, he said : "If I die, I hope that I have done my duty and that my life has not been vain and useless". Three weeks later, he was stricken with palsy, from which he never recovered. Even the devotion and medical skill of his younger brother DR. JOHN DAVY thought it best to take his brother from Rome to Geneva in order to avoid the hot Italian summer. The long journey by horse and carriage was most exhausting, and SIR HUMPHRY died at Geneva on May 29, 1829. His desire that his life might be useful was so richly fulfilled that his name will always be honored as that of a *supremely great scientist and humanitarian.*

Bleaching with Chlorine

In 1785, COUNT C. L. BERTHOLLET noticed that an aqueous solution of chlorine *destroys* vegetable colours just as the gas itself does. In the following year, he used it successfully in bleaching, and communicated his results to scientists and technical men, including JAMES WATT. WATT, in turn, carried the discovery into effect, by bleaching several hundred pieces of linen by the new process in the bleach-fields of his father-in-law near Glasgow. Others to follow WATT were PROFESSOR COPELAND who introduced it to the bleachers of Aberdeen, and DR. THOMAS HENRY began bleaching operations at Manchester.

In the early processes developed in England, France, Germany, and Austria, the bleaching agent was chlorine gas or chlorine water. To prevent its injurious effects on the respiratory system, workmen used to protect their faces with handkerchiefs moistened with dilute alkali. BERTHOLLET, however, found that the addition of alkali to the bleaching liquor deprived it of its disagreeable, suffocating odour without impairing its bleaching power. A solution of chlorine in potash was sold under the name of *Javelle Water.*

Several attempts were made to prepare a bleaching liquor from different sources, through different routes. THOMAS HENRY — a British Chemist—as early as 1788, prepared a bleaching liquor from lime and chlorine, and then PAUL KITAIBEL — a Hungarian botanist and chemist — distilled a mixture of salt, pyrolysite, and sulphuric acid and passed the liberated chlorine *("oxygenated acid of salt")* into lime-water. CHARLES TENNANT of Glasgow, who was then engaged in bleaching at Darnley prepared solid bleaching powder, in 1798, by heating a mixture of salt, pyrolusite and sulphuric acid in a leaden still and absorbing the liberated chlorine in sifted slaked lime in a leaden receiver.

The discovery of bleaching powder not only stimulated the growth of cotton, but also saved for agricultural purposes thousands of acres of arable land which had formerly been used as greenswards for the slow bleaching of textiles by the oxygen of air.

Chlorine has thus revolutionized the entire bleaching process, and a few hours accomplishes that which formerly required days; and a few hundred square-feet containing properly constructed vats takes the place of thousands of acres of land.

Disinfecting with Chlorine

A reviewer in the *"Medical Repository"* wrote in 1802 concerning GUYTON DE MORVEAU's *Treatise on the means of purifying infected air, of preventing contagion, and arresting its progress* that "The most powerful and efficacious anti-contagious agent which he knows is the *oxygenated muriatic acid gas* (chlorine). The process for preparing this differs from the ordinary muriatic acid (hydrochloric acid) gas already mentioned, only by the addition of a small quantity of black oxyd of manganese.....in powder". This anonymous reviewer (possibly SAMUEL LATHAM MITCHELL,

Editor of the *Medical Repository)* Questioned the conclusions of GUYTON DE MORVEAU and believed that aqueous solutions of potash, soda, soap, and lime were more efficacious.

Chlorine in the human body

Chlorine enters into the composition of all secretions and excretions of the human body, and gastric digestion takes place in a medium containing hydrochloric acid.

OCCURRENCE

CHLORINE IS FOUND IN NATURE, not in its highly reactive elemental state, but most, commonly in the form of the corresponding *chloride anions.* It has been estimated that ingenous rocks, which constitute about 95% of the earth's crust, contain on average 0.031% of Chlorine in the *combined state.*

The bulk of the chlorine present in sedimentary rocks and volcanic rocks takes place of-OH groups in hydroxide-bearing minerals such as *hornblendes, micas, clay minerals,* and *aluminium hydroxide.* There are otherwise known relatively few *chlorides* which may be considered as minerals in the strict meaninig of the word; the relatively insoluble ores of certain heavy metals (eg: AgCl, *horn silver;* Ag (Cl, Br), *embolite;* Hg_2Cl_2, *calomel;* CuCl, *nantokite*) are of negligible commercial importance.

However, the largest natural source of chlorine is the *sea;* out of a total average solinity of about 3.4%, sea water contains approximately 1.9% *chlorine,* mainly as sodium chloride though with smaller amounts of other chlorides, 0.0065% *bromine* (representing a *chlorine bromine* mass ratio of nearly *300 : 1*) and 5×10^{-8}% iodine. It is thus evident that *chloride ion is by far the largest dissolved constituent in the oceans.*

Isolated bodies of water in arid regions are frequently found to have a high chloride content; the Great Salt Lake of Utah, for example, contains no less than 23% sodium chloride, while the Dead Sea, with a total salinity of more than 30% contains near the surface about 3.5% calcium chloride, 8.0% sodium chloride, and 13.0% magnesium chloride.

The principal sources of chlorine of commercial significance are as follows :

Ocean-derived Deposits of such Minerals as Rock Salt, Nacl; Sylvine, KCl; Carnallite, $Mgcl_2 — KCl.6H_2O$: Kainite. $MgSO_4.KCl.3H_2O$

These deposits are widely distributed in the world, many of them being of immense proportions; countries favoured by such natural resources include : the United States, Russia, Germany, Austria, Italy, the United Kingdom, and Brazil. For the production of chlorine sodium chloride is the principal raw material, and where this is obtained from natural rock salt deposits, it may either be mined or pumped to the surface as a saturated aqueous solution.

Natural Brines Derived From Sea and Lakes

These are now a significant source of *chlorine* and the *major* source of *bromine.* Solar evaporation is commonly used to concentrate the brines and to isolate the principal dissolved ingredients. In certain areas, special *topographical* and *climatical* conditions greatly facilitate this process; such is the case in the Rann of Cutch in India, in the saline lagoons of the Black Sea and Caspian Sea, in the Sebkha-el-Melah in Tunisia, and on the Shores of inland seas and lakes such as the Dead Sea and Great Salt Lake.

Wells and Springs

Apart from the brine produced artificially by pumping water into underground salt deposits, natural brines from wells and springs are also very widespread; thus, natural waters associated with oil-fields are often relatively rich in the halide ions. Although these are most commonly the result of leaching of salt layers, it is possible that some originate from underground pockets left by ocean concentrates. Many such wells and springs are found, for example, in the United States, mainly in Michigan, Ohio and west Virginia, in parts of Russia, Israel and Italy, and many provide important natural sources of common salt, calcuim chloride and magnesium chloride.

Human Body, Animals and Plant Kingdom

In plants and animals chlorine exists primarily as the chloride ion dissolved in cell liquids, but organo-chlorine compounds, mostly of fungal origin, are also found in nature.

Chlorine is now know to be essential ingredients of biochemical processes. Human beings and animals take up chloride anions, in varying proportions, in food-stuffs, table salt and water. In common with other anions, chloride ions and other halide ions suffer diffusion in soft tissues and enter the bloodstream, whence they are removed and actively pumped into the urine by the action of the kidney. Next to urea, chlorides are the most abundant constituents of the urine.

Chloride ions exhibit certain unique functions, their concentration being regulated by active transport. Chloride ions are found mainly in the intracellular space, and make up the bulk of the anions in blood plasma. The best known active secretion of chloride in vertebrate takes place in the lining of the stomach where specialized oxyntic cells are able to secret approximately 0.17 M hydrochloric acid, which aids the digestion of food. The oxyntic cells are able to pump bicarbonate (HCO_3^-) ions into the bloodstream and hydrogen (H^+) ions into the stomach; chloride (Cl^-) ions pass from the blood to the stomach contents to maintain *electrical neutrality.*

It is also found that the distribution of Cl^- ions between plasma and the red cells of blood is similar and intimately related to that of HOC_3^- ions: as the HCO_3^- concentration varies causing the ions to diffuse into or out of the red cells, electrolytic equilibrium is maintained by a counterbalancing migration of Cl^- ions. Such shifts of Cl^- and HCO_3^- ions between the plasma and the red cells play an important role in stabilizing the pH of the blood.

Organo-chlorine compounds are also found in nature. Most of them are of fungal origin, eg. griseofulvin ($C_{17}H_{17}O_6Cl$) derived from *Penicillium griseofulvium,* and some are powerful antibiotics. Organo-chlorine compounds are also present in some red algae, and their participation in photosynthesis has been mooted.

Some principal features of the biochemistry and geochemistry of chlorine are summarized in the *Table 1* bellow :

Table 1 : Biogeochemistry of Chlorine

Location	Chlorine
Ingeneous rocks *(ppm)*	130
Shales *(ppm)*	180
Sandstones *(ppm)*	10
Limestones *(ppm)*	150
Fresh water *(ppm)*	7.8
Sea water *(ppm)*	19000
Air ($\mu g\ m^{-3}$)	1.2
Soils *(ppm)*	100
	Much higher in alkaline soils near the sea and in salt deserts. A major exchangeable anion in many soils.
Marine plants *(ppm)*	4700
Land plants *(ppm)*	2000
	Much higher in marifime [and salt desert plants.
Marine animals *(ppm)*	5000 — 90,000
	Highest in soft coelenterates, lowest in calcareous tissues.
Land animals *(ppm)*	2800
	Highest in mammalian hair and skin
Mammalian blood *(ppm)*	2900
Plasma *(ppm)*	3950
red cells *(ppm)*	1890 (1890)
atoms/red cells	$2.5X10^9$ (2.5)

PROPERTIES

CHLORINE IS ONE OF THE FOUR closely related chemical elements which have been called the ***Halogen elements.*** ***Fluorine*** is more active chemically, and ***bromine*** and ***Iodine*** are less active. Chlorine replaces iodine and bromine from thier salts. It enters into substitution and

addition reactions with both organic and inorganic materials. Dry chlorine is somewhat inert, but moist chlorine unites directly with most of the elements of the periodic system.

PHYSICAL PROPERTIES

Element number 17, chlorine ; Chemical symbol : *Cl*, is a gaseous element. It has chemical atomic weight 35.457. Chlorine belongs to the *Halogen Family* comprising of Fluorine, Chlorine, Bromine, Iodine and Astatine. It occupies the position immediately below *Fluorine* and just above *Bromine,* in the *Group VII a.* Its horizontal neighbours are *sulphur* and *Argon* in the *Period 3* of the Periodic Table.

Chlorine is a *greenish—yellow* gas that is almost three times as heavy as air. It is quite soluble in water, and is therefore never collected in the laboratory by displacing water in bottle. When cooled to 33.8°C, chlorine changes from the gaseous to the liquid state, under the pressure of one atmosphere. At room temperature it is a liquid if kept under high pressures. It is usually marketed in the liquid form in steel cylinders.

The rapid expansion of liquid chlorine with increasing temperature is an important factor in filling containers and handling liquid chlorine in pipelines. Friction loss in pipelines will be lower than that of water because of the lower viscosity of liquid chlorine. The high density of chlorine gas creates problems of dispersal in cases of spills and leaks from containers. Liquid chlorine is unique in having the highest compressibility co-efficient of any liquid element.

The *periodic* as well as *physical properties* of chlorine have been listed in the chart form on page *3* and *5* respectively.

CHEMICAL PROPERTIES

Chlorine is a member of Group *VII a* of the periodic system. While it is essentially an electronegative element, tending to go to the chloride ion of oxidation state –1, chlorine is also known in the +1, +3, +4, +5 and +7 states of oxidation. Chlorine combines directly with all but a few elements; oxygen, fluorine, nitrogen, carbon and the innert gases being exceptions, The binary compounds thus formed are called chlorides.

Reactions of Chlorine

Chlorine and Water

Chlorine reacts with water to form hypochlorous and hydrochloric acids. Chlorine hydrate, $Cl_2,8H_2O$, may crystallize below 9.6°C. A freshly prepared solution of chlorine in water is yellow in colour. After it has stood a short time, the colour of chlorine disappears and to two new substances have been formed — hypochlorous acid, HClO and hydro- chloric acid, HCl. Chlorine reacts with water according to the following equations :

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

On further standing, especially in sunlight, all the hypochlorous acid disappears and a solution of hydrochloric acid remains. The hypochlorous acid decomposes, yielding oxygen and hydrochloric acid :

$$2\,HClO \rightarrow 2\,HCl + O_2$$

If chlorine is dissolved in water and is placed immediately in sunlight hydrochloric acid and oxygen are products of the reaction :

$$2\,Cl_2 + 2H_2O \rightarrow 4\,HCl + O_2$$

The reaction may be demonstrated by filling a test tube with a solution of chlorine in water and then inverting this tube in a beaker of water. When this is placed in bright sunlight, bubbles of oxygen can be seen thorming throughout the solution in the tube and rising to the top of the test tube.

Chlorine and Hydrogen

Hydrogen burns in an atmosphere of chlorine as well as it does in oxygen. The product of the reaction is hydrogen chloride :

$$H_2 + Cl_2 \rightarrow 2\,HCl$$

If a mixture of hydrogen and chlorine is heated, or if it is exposed to bright sunlight, an explosion occurs. Practically no reaction takes place if the mixture remains in the dark.

Chlorine and Hydrocarbon

Chlorine also combines with the hydrogen part of a compound of carbon and hydrogen. Paraffin is such a compound. When a burning paraffin

candle is placed in a cylinder of chlroine, it continues to burn, but gives off a dense black smoke. Chlorine combines with the hydrogen in paraffin, forming hydrogen chloride, but since it does not read with carbon, this element, in a finely divided state, passes of unchanged. These particles of carbon cause the smoke.

If a piece of filter paper soaked in turpentine is dropped into a cylinder of chlorine, it immediately ignites and burns with a very smoky flame. Turpentine being another compound of carbon and hydrogen, and as in the case of paraffin, chlorine unites with the hydrogen in the molecule, setting free the carbon :

$$C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl$$

Chlorine and Metals

Chlorine reacts with most metals to form the chloride of the metal. If some powdered antimony is dropped into a bottle of chlorine, it ignites spontaneously, giving off a shower of sparks. The product of the reaction is antimony chloride, $SbCl_3$. :

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3$$

Hot sodium burns in chlorine, forming sodium chloride :

$$2Na + Cl_2 \rightarrow 2NaCl$$

Copper, iron, aluminium, and Zinc burn readily in chlorine if they are warned :

$$Cu + Cl_2 \rightarrow CuCl_2$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

$$Zn + Cl_2 \rightarrow ZnCl_2$$

Chlorine and Non-metals

Chlorine reacts directly with sulphur, forming sulphur monochloride, S_2Cl_2, dichloride, SCl_2 and tetrachloride, SCl_4 :

$$2S + Cl_2 \rightarrow S_2Cl_2$$

$$S + Cl_2 \rightarrow SCl_2$$

$$S + 2Cl_2 \rightarrow S\,Cl_4$$

It reacts with phosphorus, yielding the trichloride, PCl_3, or the penta chloride, PCl_5 :

$$2P + 3Cl_2 \rightarrow 2PCl_3$$

$$2P + 5Cl_2 \rightarrow 2PCl_5$$

Chlorine and Halogens

Chlorine reacts with fellow halogen, iodine, forming the monochloride, ICl, and the trichloride, ICl_3 :

$$I_2 + Cl_2 \rightarrow 2\,ICl$$

$$I_2 + 3Cl_2 \rightarrow 2\,ICl_3$$

The products of the interaction of chlorine with bromine are monochloride, BrCl, or trichloride, $BrCl_3$

$$Br_2 + Cl_2 \rightleftharpoons 2\,BrCl$$

$$Br_2 + 3Cl_2 \rightarrow 2\,BrCl_3$$

Similarly, chlorine reacts with fluorine to form ClF, ClF_3, or ClF_5

$$Cl_2 + 5F_2 \rightarrow 2\,ClF_5$$

Chlorine and Gases Other than Halogens

Chlorine does not react directly with nitrogen, but excess chlorine or hypochlorous acid will react with ammonium salts in acidic solution; producing nitrogen trichloride, NCl_3, an oily liquid which is highly explosive :

$$3\,Cl_2 + NH_4Cl \rightarrow NCl_3 + 4\,HCl$$

In dilute, equimolar solutions of ammonia and hypochlorite, the unstable chloramine (chloramide), NH_2Cl, is formed :

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

Chlorine, when reacts with excess of ammonia, yields hydrazine, N_2H_4.

$$4\ NH_3 + Cl_2 \rightarrow 2\ NH_4Cl + N_2H_4$$

Hydrazine is an important reducing agent which is used as a fuel in rocket propellants.

Chlorine does not react directly with oxygen although the following oxides have been described in the chemical literature: Cl_2O, ClO_2, ClO_3, and Cl_2O_7. All are characterized as being unstable, decomposing with varying degrees of explosive violence.

Chlorine and Organic Compounds

Chlorine reacts with many hydrocarbons, replacing one or more hydrogen atoms and forming hydrogen chloride as a by-product. Thus, with methane the initial product is methyl chloride :

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCL$$

By successive substitutions dichloromethane, chloroform and carbon tetrachloride are formed :

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_3 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

With other unsaturated hydrocarbons, chlorine produces the saturated chloride, such as ethylene dichloride from ethylene :

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Chlorine reacts with carbon disulphide forming carbon tetrachloride by replacement of sulphure :

$$CS_2 + 3\ Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

NUCLEAR PROPERTIES

There are two stable isotopes of chlorine, of atomic mass 35 and 37. These occur to the extent of approximately 75.4% and 24.6%, respectively,

in the chlorine containing compounds. Thus, the average atomic weight of this element is 35.457.

In addition, there are five radioactive isotopes of atomic mass 33, 34, 36, 38, and 39. The half life of these range from approximately 2.8 seconds for the isotope of atomic mass 33 to 4.4 x 10^5 years for the isotope of atomic mass 36.

PHYSIOLOGICAL PROPERTIES

When chlorine is inhaled, the mucous membranes of the nose and throat become irritated. The effects are those of a bad cold in the head. If inhaled in large quantities, chlorine is poisonous and may result in death.

TO BE CONTINUED

in childbirth. He also discovered the anesthetic properties of *chloroform* by experimenting on himself. (7).

12. A French epothecary; professor in the school of pharmacy, Paris; who alongwith others discovered chloroform in 1831. (9).
13. A German Chemist, who described the preparation of hydrogen chloride from common salt and oil of vitriol. (7).
14. An English Scientist of Glasgow, who patented the method of preparing *"bleaching powder"* by absorbing chlorine in dry hydrated lime. (7).
15. Animal feed additive derived from the agricultural waste or made synthetically from trimethylamine and ethylene oxide. (7 + 8).
16. A clay mineral which is widespread in argillacecus sedimentry rocks and in certain soils. (8).
17. A commercial mixture of isomers of 1: 2: 3: 4: 5: 6–hexachlorocyclohexane, which is used as an insecticide. The γ (gamma) isomer is toxic. (7 + 12).
18. An abriedged form of Benzene Hexa Chloride, by which name the product is popularly known in the market. (3).
19. A water solution of chloride is titrated directly with standard silver nitrate using a few drops of 0.02 *M* potassium chromate as indicator. Name the scientist after whom this method is popularly known. (4).
20. An *antihistaminic* agent with good therapeutic efficacy and low incidence of side effects. (16 + 7).
21. The scientist who observed and put into practice the bleaching properties of chlorine gas and its solution in water. (10).
22. Charles Tennant of Glasgow prepared a powder from salt, pyrolusite and sulphuric acid using slaked lime as a chlorine absorber. This powder is used for textile bleaching. Name it.
23. A German chemist who, alongwith Soubeiran, discovered Chloroform. (6).
24. The physicist and chemist who *first* prepared tetrachloroethylene by the thermal decomposition of hexachloro–ethylene. He also *first* prepared BHC in 1825. (7).
25. The solution of chlorine in caustic potash.. Give its ancient name (3 + 2 + 7)
26. A broad spectrum *antibiotic* and *antiprotozoan* which suppresses the growth of most *Gram-positive* bacteria, many *Gram-negative* bacteria, spirochetes, amebae, and certain large viruses. (17).

27. A synonym for *rock salt.* It is a chlorine mineral occuring in New York, Gulf Coast, Great Salt Lake, New Foundland, Sambhar etc. (6).
28. A short form of a synthetic thermoplastic polymer, used in piping, toys, rain coats, magnetic tapes, shoes, food-containers, tennis court playing surfaces, phenograph records, etc. (3).
29. A wide-spectrum antibiotic which has anti-bacterial activity including rickettiside, certain viruses and many bacteria; and which is absorbed rapidly from the *gastro-intestinal tract.* (15).
30. One of the horizontal neighbours of chlorine, which is an inert element, used in specialized light bulbs (neon, fluorescent and sodium vapour). (5).
31. The *trade-name* of chlortetracycline, under which it is popularly sold. (10).
32. An unit process through which chlorine is introduced into an organic nucleus to form a series of chloro-compounds, which occupy a unique and important place in the economy of chemical industry. (12).
33. *"Knockout drops"* — transparent, colourless – crystals, with aromatic, penetrating, slight by acrid odour. Used in medicine as sedavive, and also as a raw material for DDT. (7 + 7).
34. The Swedish pharmacist who discovered chlorine in 1774. (7).
35. A colourless liquid used in the manufacture of neoprene. (11).

VERTICAL LEGEND

1. An aqueous solution of chlorine having clear, yellow colour which deteriorates on exposure to air and light. used as deodourizer, disinfectant and antiseptic. (8 + 5).
36. A compound which occurs widely in nature, both as deposits left by ancient seas and in the ocean, where its average concentration is 2.6%. (6 + 4).
37. The Chemist who *first* prepared methylene chloride by chlorinating methyl chloride in sunlight, in 1840. He also discovered carbon tetra-chloride in 1839. (8).
38. The solution of chlorine in caustic soda. Give its ancient name. (3 + 2 + 10).
39. A group of compounds. Fastest growing branch of heavy chemical industry. Used in solid properllents, for missiles match industry, and pyrotechnics. (9).

40. The author and chemist who prepared Ethyl chloride from the *spirit of of common salt* (hydrochloric acid) and the *spirit of wine* (ethyl alcohol). (9).

41. The process through which almost entire quantity of chlorine is produced from fused chlorides or aquecus solutions of alkali metal chlorides. (12).

42. The entire grcup of elements : fluorine, chlorine, bromine iodine and astatine belong to particular *family.* Name this family. (7+6)

43. A colourless, hygroscopic liquid and a strong oxidizing agent used in medicine, electroplating and electropolishing and analytical chemistry in non-aqueous titrations. (10+4)

2. The *green plant pigment* essential to photosynthesis. Used as colourant for soaps, oils, fats, waxes, liquors, confectionery : as a sensitizer for colour film; as a tooth-paste additive and in medicine. (11).

44. A synthetic thermoplastic polymer. White powder or colourless granules. Used in piping, conduits, gutters, raincoats, toys, gaskets, garden hose, electrical insulation. shoes, magnetic tapes, cosmetics & toiletries containers, tennis court playing surfaces, flooring, synthetic turf, phonagraph records, etc. (9+8).

45. One of two scientists who suggested that *"oxy-muriatic acid"* was an element. He was a swedish subject. (7).

46. The antibiotic discovered by BENJAMIN DUGGAR in 1948. It was designated a *specific name* because of two reasons : first, because of the golden yellow pigment that was produced in the moist substrate *mycelium* and, secondly, because the antibiotic itself was faintly golden yellow in colour. (10).

47. An English industrialist who exploited the bleaching properties of chlorine by bleaching several hundred yards of linen in the bleach fields of his father-in-low, near Glasgow. (4).

48. An epoxide with chloroform-like odour, employed in the manufacture of epoxy and phenoxy resins, glycerol, etc. (14).

3. One of two scientists, who suggested that *"oxy-muriatic acid"* was an element. He was also a swedish subject. (3+6).

49. An abriedged form of a compound whidh is used as a plant growth regulant. It is a chlorine chloride derivative. (3).

50. The English scientist who first liquefied the chlorine gas prepared by Scheele. (4).

51. An yellow, gaseous hydrocarbon, C_4H_4, made by passing acetylene through a quartz tube at 750°C. It has the name analogy with CHLORINE. (8).

52. The French Scientist who coined the word : *"acide muriatique"* from which the english name muriatic acid is derived. He is considered as the *"Father of Modern Chemistry"*. (9).

53. An *obsolete name* for hydrochloric acid. (8+4).

54. A uniform solution of essentially constant composition containing 96.5% wate and 3.5% ionized salts, associated compounds, elements and ionic complexes. Good source of sodium chloride, bromine, magnesium, and fresh water. (3+5).

55. A clear colourless, or slightly yellow colours pungent solution of hydrogen chloride gas in water. Used in acidizing of petroleum wells, food processing, pickling and metal cleaning, alcohol denciturant, etc. (12+4).

56. A Colourless crystalline or white to slightly off-white powder with aromatic odour used as a house-hold insecticide. Popularly known by its short form only. (3).

18. One of fhe two *vertical neighbours* of chlorine. (7).

57. A colourless liquid, with sweetish odour, yielding vapours 5.3 times heavier than air. *Non-combustible,* Can not be used to extinguish fire. Used in refrigerants, propellants, metal degreasing, agricultural fumigant, etc. (6+13).

58. A paraffin oil or wax in which some of the hydrogen atoms have been replaced by chlorine. Used in high-pressure lubricants, as flame retardant in plastics and textile, as plasticizer for PVC in polyethylene sealants and in detergents. (10+9).

59. A white, crystalline odourless powder with *very bitter taste,* Employed for the control of acute attacks of *vivax malaria* as well as *falciparum malaria.* (11).

TO BE CONTINUED

Chlorine was one of the first elements to be weighed in the mass spectrograph, and it was found by F. W. ASTON, a student of J. J. THOMSON, to possess two isotopes : 35_{Cl} and 37Cl. At this time (about 1920), British Industry utilised either the 'Smith Method' or the 'Muspratt Method' to produce chlorine. When an excited young industrial scientist told this superiors of the newly-developed mass spectrograph and the existence of 35Cl and 37Cl, he was calmly informed " We in Liverpool have known that there are two chlorines for years. There is Tom Smith's Chlorine and there is Max Muspratt's Chlorine ! "

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C. Uberoi; *Science Today,* **13** (4), 13, (Oct., 1978).

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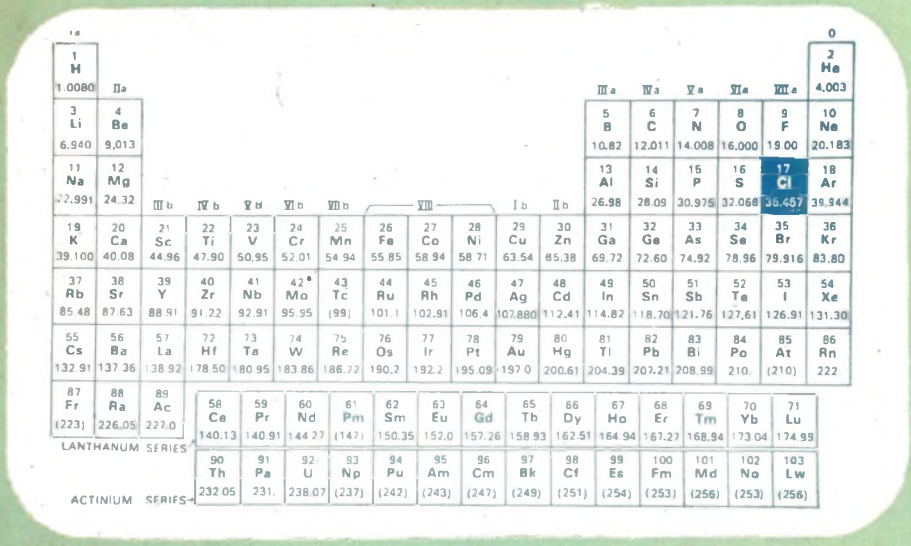
THE STORY OF THE ELEMENTS

Chlorine

(Part II)



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1 H 1.0080	IIa																2 He 4.003
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32	IIIb	IVb	Vb	VIb	VIIb						13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.92	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 208.99	84 Po 210.	85 At (210)	86 Rn 222
87 Fr (223)	88 Ra 226.05	89 Ac 227.0															

LANTHANUM SERIES	58 Ce 140.13	59 Pr 140.91	60 Nd 144.27	61 Pm (147)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
ACTINIUM SERIES	90 Th 232.05	91 Pa 231.	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (256)

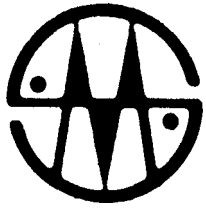
November—December 1978

SARABHAI M CHEMICALS

THE STORY OF THE ELEMENTS

Chlorine

(Part Two)



SARABHAI M CHEMICALS
BARODA

CHLORINE

[Part Two]

MANUFACTURE

CHLORINE IS MANUFACTURED almost entirely by electrolytic methods from fused chlorides or aqueous solutions of alkali metal chlorides. In the electrolysis of brines, chlorine is produced at the anode, and hydrogen, together with sodium hydroxide and potassium hydroxide, at the cathode. As the anode and cathode products must obviously be kept entirely separate, many ingenious cell designs have been developed and refined. Except for an early period when the bell-jar was used, all these designs have been either variations on a type of diaphragm, or else variations on a mercury intermediate electrode.

Diaphragm Process

In the diaphragm process, brine is fed continuously and flows from the anode compartment through an asbestos diaphragm backed by an iron cathode. To minimize back-diffusion and migration, the flow rate is always such that only part of the salt is converted. The hydrogen ions are discharged from the solution at the iron cathode, forming hydrogen gas and leaving hydroxyl ions. This catholyte solution, containing caustic soda and unchanged sodium chloride, is evaporated to obtain the caustic soda, In the course of the evaporation the sodium chloride precipitates, is separated and redissolved, and sent back to the electrolysis.

Intermediate Mercury Electrode Process

In the intermediate mercury electrode process the cation, after discharge, forms an alloy or amalgam with mercury. This amalgam flows or is pumped to a separate chamber in which it is allowed to react electrochemically, most often with water, to form hydrogen and a comparatively strong caustic soda solution containing almost no sodium chloride.

Historical

Chlorine was first prepared by K. W. SCHEELE, in 1774, from hydrochloric acid and manganese dioxide : $MnO_2 + 4HCl \rightarrow Cl_2 + MnCl_2 + 2H_2O$. HENRY DEACON produced chlorine from hydrochloric acid and oxygen at 400°C with copper chloride absorbed in pumice stone as a catalyst (1868) : $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$. The first ever eletrolytic process was patented in 1851 by CHARLES WATT in Great Britain. Electrolytic chlorine was, however, first produced successfully on a commercial scale about 1890 : The raw material used here is salt and water : $2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$. H. Y. KASTNER (U.S.A.) and C. KELLNER (Austria) brought about revolution in the electrolytic production of chlorine.

Electrolytic Process

In the mid-20th century, the electrolysis of brine was the major source of industrial chlorine. A minor source was the electrolysis of fused sodium chloride, wherein metallic sodium is the primary product and chlorine a by-broduct.

Electrolytic chlorine was first produced successfully on a commercial scale about 1890. The following half century saw an enormous increase in the amount of chlorine produced. Technical improvements greatly increased the efficiency of production, but the process remained basically unchanged. The raw materials are salt (NaCl) and water; the products chlorine, sodium hydroxide and hydrogen. The change which is brought about by electrical energy may be represented by :

$$2\ NaCl + 2H_2O \rightarrow Cl_2 + 2\ NaOH + H_2$$

Although the electrolysis of salt produces equivalent amounts of both chlorine and caustic soda, the chlorine is regarded as the primary product and the caustic soda a by-product because, without a market for chlorine, the caustic soda so produced can not compete economically with caustic from the ammonia-soda process.

Two distinct types of cells are employed, the diaphragm cell (and the mercury cell. It both the cells, the electrolyte is a strong solution of salt (brine). Calcium and magnesium ions are precipitated from the brine before it enters the cell by addition of sodium carbonate, since these ions would otherwise precipitate in the cell and interfere with its operation. Both types of cells employ graphite anodes but differ in the cathode material. Iron cathodes are generally used with the diaphragm-type cell, while a mercury cathode is the distinctive feature of the mercury-type cell. The reaction at a graphite anode is the liberation of chlorine gas : $2\ Cl^- = Cl_2 + 2\ e$. Small amounts of oxygen usually accompany the chlorine, thus reducing the efficiency of operation.

Diaphragm Cell

In a diaphragm cell, hydrogen is discharged from the iron cathode. Discharge of sodium does not occur in the presence of water, for the potential required to discharge sodium is much greater than that at which hydrogen is set free. The hydrogen comes from the water, leaving hydroxyl ion in solution :

$$H_2O + 2\ e = H_2 + 2OH.$$

To avoid the mixing of the two, both the cathode solution and the anode solution are kept separate with a diaphragm made of asbestos paper. The cathode liquors average 110 to 120 g NaOH per litre and 140 to 170 g NaCl per litre. An outlet above the cathode allows the hydrogen to

escape or to be collected. The anode section generally has a concrete cover with an opening for collection of the chlorine.

Factors influencing the design of cells are the initial cost, life period, purity of product and efficiency with which electrical energy is utilized.

Some of diaphragm-type cells in common use at mid-20th century were the Allen-Moore and Hooker type S (u.s.), the Hazgreaves-Bird (British), Krebs (French), Billiter (German) and the Vorce (U.S.).

Mercury Cell

In the mercury - type cell sodium is discharged into the mercury cathode at the bottom of the cell, and no hydrogen is evolved. Mechanical agitation moves the amalgamated mercury to a separate compartment of the cell where it is made the anode, causing the sodium to go back into the solution as sodium hydroxide, while the hydrogen is discharged from an ion cathode. The over-all reaction is the same as with the iron cathode-type cell.

The advantage of the mercury-type cell is that the caustic soda solution is free from chloride and may be produced at as high as 50% concentrate in the cell, while in the other cells the caustic soda is more dilute and considerable chloride must be separated to prepare the sodium hydroxide for sale. The disadvantage of the mercury-type cell is the high cost of mercury. The efficiencies reported are about the same as for the diaphragm-type cell.

The original mercury-type cells were developed by H. Y. KASTNER (U.S.) and C. KELNER (AUSTRIA). Modern versions of these Kastner-Kelner cells are the Krebs, Mathieson, I. G. Farben Industrie and Imperial Chemical Industries Cells.

Distribution

Chlorine from the cells is freed from the moisture by the action of concentrated sulphuric acid, cooled and liquefied by compression. The liquefied chlorine is sold in steel cylinders and tank cars.

APPLICATIONS

THE RAPID ADVANCEMENT OF the chemical industry in the country as well as in the world has enhanced the production of chlorine at very high levels in the industrially advanced countries.

The growth of inorganic and organic chemicals such as metallic chlorides, hypochlorites, bromine, chloro solvents, carbon tetrachloride, chlorinated hydrocarbons, ethylene glycol, ethyl fluid, lubrication aids, solubilizing starch, DDT, Vinyl chloride, BHC, Chloro acids, Chloro benzenes, chlorotoluenes and many intermediates for the preparation of dyes, synthetic drugs and and plastics industries has placed heavy demands on chlorine industry in developed countries.

The most significant quantities of chlorine are used for the production of organic chemicals including solvents, refrigerants, plastics, plasticizers, detergent intermediates, insecticides and dyes. Important quantities of chlorine are also used for the production of inorganic chemicals such as synthetic hydrochloric acid, bromine, bleaching powder, sodium hypochlorite and metal chlorides. Next in the order of chlorine consumption comes the pulp and paper industry where chlorine is used for bleaching wood-pulp, waste-paper and other paper making fibres as well as for the control of lime.

The other important uses of chlorine include disinfection of swimming pools and bathing beaches, sterilization of utensils and containers in dairies, breweries, carbonated beverages plant, public food and beverage dispensers, packing and poultry houses, controlling odours in fertilizer plants, bleaching of cotton, rayon linen, rags, shellac, flour, etc. Sanitation, i.e., control of bacteria, micro-plant and animal life in municipal and industrial waters and sewage waste also consume huge quantities of chlorine or its derivatives.

These combined uses have resulted in making chlorine one of the most essential material in both war and peace.

Utilization of chlorine & its compounds in chemical industry

Chlorine is often referred to as the back-bone of the modern chemical industry. It plays a dynamic role in the industrial development, which

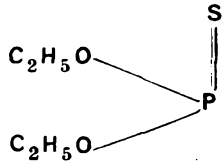
can be seen from the variety of industries that consume it as raw material as shown in the Table below.

TABLE : UTILIZATION OF CHLORINE AND CHLORINE COMPOUNDS IN CHEMICAL INDUSTRY

Name of Industry	Chlorine Products	Advantages & Uses
Pulp and Paper	Hypochlorite and bleaching liquors	Bleaching action and bactericidal action during stocking of pulp.
Sugar	Electrolytic chlorine	(a) Bleaching and (b) Clarification of juice by discharging the electric potential of the colloids.
Plastic	PVC and allied copolymers and also catalyst chlorides.	For insulators and industrial pipe line, coating of steel sheets for use as substitutes for tin sheets and galvanized iron sheets.
Food canning	Mono sodium glutamate.	Food seasoning.
Rubber and elastomers	(a) Neoprene or chloroprene	Due to its high chlorine content, it will not support combustion and hence used for making conveyor belts in mines where flames resistance is prime requirement.
	(b) Hypolan rubber by substituting chlorine and sulphonyl group into polyethylene. Sulphonyl group provides active centres for cross linking of vulcanisation.	Gives a product which is a flexible rubbery polymer unlike the stiff plastic parent.

Name of Industry	Chlorine Products	Advantages & Uses
	(c) Chlorinated paraffin derivatives	Compounding agents for elastomers.
	(d) Chlorinated rubber	Practically insoluble in water, alcohol, petroleum ether, ether and mineral oils. Used in corrosion resistant paints and varnishes.
Ion exchanger	A highly polar rubber derivative obtained by heating chlorinated rubber (64% chlorine content) with ammonia and a sulphonated type of emulsifying agent in an autoclave for 3 hrs at 150°C. Some chlorine atoms are replaced by amine group.	Ion-exchange purposes.
Detergent industry	(a) Alkyl benzene from an alkyl side chain compound which may be an olefin or an alkyl halide (chlorinated kerosene also may be used).	Starting point for detergents competitive to soap products.
	(b) Ethylene oxide, propylene oxide.	Starting point for surfactants.
Refrigerants	Freons	Refrigeration and Cryogenics.
Motor spirit	Lead tetraethyl	Anti-knocking agent.

Name of Industry	Chlorine Products	Advantages & Uses
Solvents	Chlorinated organic solvents like chloromethanes.	(a) Similar to the parent hydrocarbons in their general chemical properties and solvent behaviour.
	Chloroethanes, chloroalkyl benzenes.	(b) non inflammable in character.
	Chloroethylenes, etc.	(c) more active and powerful.
		(d) slightly more polar with higher electrical conductivities and dielectric constants making a good solvent for certain more hydrophilic substances.
Fertilizers	Dicalcium phosphate, phosphoric acid, hydrochloric acid and phosphate rock.	Eliminates the use of sulphuric acid otherwise necessary.
	Ammonium chloride from hydrochloric acid and ammonia. For every ton of Cl_2, 0.028 ton of hydrogen is produced in electrolytic cell.	Can replace ammonium sulphate and also bring into use the hydrogen coproduct of electrolysis.
Insecticides	DDT, Gammexane BHC from chlorobenzene; toxaphene from turpentine (60.5% chlorine) (also a fumigant)	Contact insecticides and fumigants.

Name of Industry	Chlorine Products	Advantages & Uses
	phosphate insecticide 	
Weed-killer and herbicides	2:4 – D (D = dichlorophenoxy-acetic acid) and other substituted compounds.	A low cost method of selectively destroying weeds. In low concentrations of 1 — 3 ppm, it could gently speed up plant growth.
Disinfectants, Germicides and antiseptics	Chloramines.	For break point chlorination and improving taste and odour of water.
Defence	Chlorates and perchlorates, mustard gas, diphosgene, diphenyl arsenic chloride, hexachloroethane.	Propellents and fuses. Irritant gas. Smoke generating gas.

COMPOUNDS

HIGH REACTIVITY OF CHLORINE makes it enter into *substitution* and *addition reactions* with both organic and inorganic materials. Chlorine as such, or in the form of one of its several active combinations is used principally in the manufacture of a number of inorganic and organic chemicals.

In an industrialised country, one can not imagine chemical industry

without chlorine. The final products from chlorine are found in almost all branches of industry and daily life. The very many uses of chlorine, however, do not allow to mention all possibilities for its use and, therefore, a brief report is given where chlorine is mainly needed in inorganic and organic chemistry and what the manufactured products are used for. Here, various usabilities of chlorine and the manufacture of chlorine compounds are given by some selected examples.

For the ease of classification, chlorine compounds have been divided into three major groups : *Natural Compounds, Inorganic Compounds* and *Organic Compounds.*

NATURAL COMPOUNDS

Many inorganic chlorides are quite soluble in water. As a result, they are leached out of land areas by rain and ground water to accumulate in the sea or in the lakes that have no outlets. Solar evaporation produces large deposits of salts in land-locked areas. Similar evaporation in the past is responsible for vast underground deposits of rock salt and brines which may be found in Michigan, Central New York and the Gulf Coast of Texas in the USA; Stassfurt in Germany; and Sambhar, Kharaghoda and Dharasana in India. These deposits are mainly of sodium chloride, the supply of which is unlimited for practical purposes.

Sodium Chloride

Both the *Old* as well as *New Testaments* abound in literal and figurative allusions to salt : *"Ye are the salt of the earth"; "Have salt in Yourselves and have peace one with another".*

It is almost impossible to write a chronological history of the discovery, production and early uses of salt. These probably developed as slowly as mankind itself. Sodium chloride or salt, NaCl, has probably been with us from the beginning of geologic time, and has probably always been necessary either directly or indirectly through all stages of the evolution of living things.

Salt is undoubtedly considered the *first chemical compound* (besides water) which attracted the attention of man in his progress *from Savagery to*

civilization. It is the only stone eaten directly by a man,- and is called *"The Edible Gem".*

The word *salt* is derived from the Latin *Sal* (=salt). It is recovered by the *three* principal methods : *Shaft mining* - a method similar to *coal mining,* where is salt is recovered by applying such well established techniques as cutting, side-shearing, drilling, blasting, loading and transporting. In *solution mining,* water is pumped into the rock salt deposit, dissolving the salt and pumping out the salt brine to the surface. Salt is recovered from this brine after it is made free of impurities *Solar evaporation* is *historically* the oldest process. Worldwide, solar salt accounts for close to 50% of the world's salt production.

There are literally thousands of uses for salt, and it is possible to discuss the major ones.

Technologically, the most important reactions of salts are those in which it is used as a starting material for the production of other materials, many of which are used to produce still other chemicals. Salt is the raw material for almost all chemicals containing *sodium* and *chlorine.*

An increasingly important use of salt is for dust control and snow and ice removal. Another highway use of salt is for stabilization of secondary roads.

Salt is used in the meat, canning, baking, fishing, dairy and other food-processing industries. In the field of agriculture, salt provides the ideal carrier for supplying minerals and trace elements in the diet of animals. Salt is used in loose form or in pressed blocks.

A rapidly growing use of salt is for regeneration of ion-exchange resins used to produce soft water. The use of salt is also important in leather tanning, in textile dyeing, in soap making, in pulp and paper manufacturing, in metallurgy, in ceramics, in rubber manufacturing, in refrigeration, and in the petroleum industry.

Calcium Chloride

Calcium chloride, $CaCl_2$, is usually obtained from brines or as a by-product of chemical processing. Its main uses are in road treatment, coal treatment, concrete conditioning and refrigeration.

INORGANIC COMPOUNDS

Wet chlorine reacts with metals to form chlorides, most of which are soluble in water. It also reacts with sulphur and phosphorus, and with other halogens.

Sodium Hypochlorite

Solid sodium hypochlorite, NaOCl, can be prepared in anhydrous form in better than 90% purity, but usually decomposes completely within a few days, sometimes with explosive force. It also forms a monohydrate, mp 75 – 80°C, which is difficult to prepare in pure form. The hydrate, NaOCl. 2.5 H_2O, is tetragonal and may be prepared in separatable crystals, but has insufficient stability for commercial use. The pentahydrate has a melting point of 27°C, so it can only be shipped under refrigeration. If the compoud is kept at ice temperatures, it is adequately stable, and may be used as a process intermediate.

Bleach Liquor

Bleach liquor is a solution of calcium hypochlorite and calcium chloride, generally containing 85 – 100 g/litre of available chlorine.* This is usually diluted to approximately 20 g/liter before use.

* AVAILABLE CHLORINE : In dealing with these compounds, the term "available chlorine" is commonly used. This is based on the oxidizing power of the material and is shown by its ability to liberate iodine from the acidified iodide solution, where one hypochlorite ion is equivalent to two atmos of elemental chlorine :

$$Cl_2 + 2HI \rightarrow I_2 + 2HCl$$

$$OCl^- + 2HI \rightarrow I_2 + Cl^- + H_2O$$

In analysis, therefore, the "available chlorine" content accounts for all the chlorine used to prepare the solution, including that which reacted to form chloride.

Practically, all hypochlorite bleach solutions used in pulp and paper operations are prepared from bleach liquor.

Bleaching Powder

True bleaching powder may be considered to contain a distinct compound

rather than a mixture of compounds. An approximate formula would be $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$, although marked variations are frequent. Extra water of hydration in quantities to total 16–17% is frequently present.

The introduction of bleaching powder by CHARLES TENNANT in 1798 provided a means of shipping *available chlorine,* so that it would be possible to use the compound at a point distant from its manufacture.

True bleaching powder is a dry powder, not markedly hygroscopic. It has sufficient stability to be widely distributed, but could not be shipped into countries with warm climates without serious losses in stability.

Bleaching powder is used in large quantities in the textile and paper Industries to whiten a textile or a paper by chemical action. It also found applications for house-hold bleaching purposes. Usually, bleaching powder is employed on the industrial scale only.

Sodium Chlorite

Sodium chlorite, $NaClO_2$, is produced by reduction of calcium chlorate by hydrochloric acid to chlorine dioxide, followed by absorption and reduction with caustic and peroxide :

$$Ca(ClO_3)_2 + 4HCl \rightarrow 2ClO_2 + Cl_2 + CaCl_2 + 2H_2O$$

$$2ClO_2 + 2NaOH + H_2O_2 \rightarrow 2NaClO_2 + O_2 + H_2O$$

The use of sodium chlorite permits controlled bleaching, and it is stable unless heated. The corresponding acid for chlorites is *chlorous acid,* $HClO_2$. Acidified sodium chlorite bleaching bleaches are very popular for cellulose and textile processing.

Potassium Chlorate

Potassium chlorate, $KClO_3$, is a white powder or transparent, colourless, monoclinic crystals. It is poisonous and may explode on contact with combustible substances.

It is prepared by direct electrolysis of potassium chloride incells in which the products of electrolysis are allowed to mix.

$$KCl + 3H_2O \rightarrow KClO_3 + 3H_2$$

Graphite anodes are used, and cooling coils or jackets are provided to remove heat. The effluent may be cooled to crystallize out potassium chlorate. Potassium perchlorate is mainly used in the manufacture of matches.

Sodium Chlorate

Sodium chlorate, $NaClO^3$, is a colourless, odourless, cubic or trigonal, crystal material.

It is prepared by the electrolysis of a hot sodium chloride solution. Chlorine liberated at the anode is allowed to react with OH^- as in equation.

$$3Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$$

Hydrogen is liberated at the cathode, and the products of electrolysis are allowed to mix. The overall reaction, then, is

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$$

There is a heavy demand for sodium perchlorate mainly because of the widespread adoption of the *chlorate-derived* chlorine dioxide bleach by the pulp and paper industry. Although wood pulp bleached with chlorine dioxide has superior brightness over pulps bleached with other reagents, the strength of the cellulose fiber is not degraded, thus a whiter and stronger paper is obtained with chlorine dioxide. However, because of its hazardous properties, chlorine dioxide can not be shipped. It is, therefore, generated from sodium chlorate by the pulp producers at their individual bleaching plants. Sodium chlorate is also used in the production of perchlorates.

Ammonium Perchlorate

Ammonium perchlorate, NH_4ClO_4, is a white crystalline compound. It is prepared by electrolysis of sodium chlorate, using platinum electrodes, followed by conversion to ammonium perchlorate by ammonium chloride.

$$4\ NaClO_3 \rightarrow 3\ NaClO_4 + NaCl$$

$$NaClO_4 + NH_4Cl \rightarrow NH_4ClO_4 + NaCl$$

Ammonium perchlorate is extensively used as an oxidizer in solid prope-

llants for jets and rockets. It is also used in the manufacture of explosives and pyrotechnics. It also finds applications as etching and engraving agent and an analytical reagent.

The corresponding acid is perchloric acid, $HClO_4$, a colourless, fuming liquid that can be used as an oxidizing agent.

Hydrogen Chloride

Hydrogen chloride, HCl, is a colourless, pungent, poisonous gas which liquefies at 82 atm at 51°C. This acid, known as hydrochloric or muriatic acid, is produced by the LeBlanc process.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$

It is also a by-product of many organic chlorinations. It can also be made by direct reaction of chlorine and hydrogen in an open combustion chamber submerged in cooled, aqueous hydrochloric acid solution. Constant boiling solutions at 760 mm pressure contain 20.24% HCl, whereas a saturated solution at 15°C contains 43.4% HCl and has a specific gravity of 1.231.

It is highly toxic by ingestion and inhalation; strong irritant to eyes and skin.

It is employed in variety of uses, such as : acidizing (activation) of petroleum wells; chemical intermediate; ore reduction; food processing (corn syrup, sodium glutamate); pickling and metal cleaning; industrial acidizing; general cleaning, e.g., of membranes in desalination plants; and alcohol denaturant.

Aluminum Chloride

Aluminum chloride, $AlCl_3$, is an anhydrous, white, deliquescent, hexagonal crystalline substance. Either scrap aluminum or the oxide *(bauxite)* may be chlorinated scrap or pig aluminum is melted at 660°C, chlorinated, and aluminum chloride vapour is condensed. Bauxite is calcined at 980°C, mixed with coal or coke, pulverized, briqueted with asphalt, recalcined to 18% carbon, heated to 870°C in a bauxite-lined vertical kiln, and chlorinated.

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$$

Aluminum chloride is a catalyst for the production of cumene, styrene, and isomerized butane. Of the aluminum chloride, 70% is used in refining and catalysis in the petroleum industry, 20% for manfuacture of dyes, and 10% for other purposes. It serves as a nucleating agent for titanium dioxide pigments.

Titanium Tetrachloride

Titanium tetrachloride, $TiCl_4$, is a clear, colourless liquid. Production of titanium metal became of considerable interest in the 1950s for miliatary uses. This required production of titanium tetrachloride from chlorination of *rutile* (TiO_2) or *ilmenite* ($FeO.TiO_2$).

$$TiO_2 + 2\,Cl_2 \rightarrow TiCl_4 + O_2$$

Titanium tetrachloride is used as a polymerization catalyst, and as a smoke-screen agent, or for sky writing. It is also employed to prepare titanium metal and titanium salts; in the manufacture of mordant dyes; to produce iridescent effects in glass and to prepare titanium pigments.

Zirconium Tetrachloride

Zirconium tetrachloride, $ZrCl_4$, is a colourless lustrous solid. Zirconium technology came into prominence in the late 1950s.

Zirconium chloride is manufactured through several routes : (a) by chlorination of zirconium carbide or zirconium cyanonitride, (b) by the action of chlorine and carbon on the ores, *zircon* ($ZrSiO_4$) or *Zirconia* (ZrO_2), (c) by treating ores with carbon tetrachloride or phosgene, and (d) by the action of hydrochloric acid on zirconium hydroxide.

It is used in various fields : as a source of the pure zirconium metal; as a reagent in analytical chemistry , in the preparation of water repellents for textiles , as a tanning agent , as a catalyst, and in the preparation of other zirconium compounds.

Phosphorus Trichloride

Phosphorus trichloride, PCl_3 is a clear, colourless, fuming liquid, decomposing rapidly in moist air. It is soluble in ether, benzene, carbon disulphide and carbon tetrachloride.

Phosphorus trichloride is prepared by passing a current of dry chlorine over gently heated phosphorus, which ignites. The trichloride, admixed with some pentachloride, distills over. A small amount of phosphorus is added and the whole is distilled.

It is used in making phosphorus oxy-chloride. It is also used as an intermediate for organophosphorus pesticides, surfactants, phosphites, gasoline additives, plasticizers and dyestuffs. Its other uses are : as a catalyst, for preparing rubber surfaces for electro-deposition of metals, and as an ingredient of textile finishing agents.

Phosphorus Pentachloride

Phosphorus pentachloride, PCl_5, is a slightly yellow, crystalline mass having irritating odour. Ordinarily it sublimes over without melting at 160–165°C. Phosphorus pentachloride is soluble in carbon disulphide and carbon tetrachloride.

It is prepared by the action of chlorine on phosphorus or phosphorus trichloride. It finds use as a catalyst and as a chlorinating and dehydrating agent.

Phosphorus Oxychloride

Phosphorus oxychloride, $POCl_3$, is an important reagent in organic chemical synthesis. It is a clear, colourless, fuming liquid with characteristic pungent odour.

Chlorine is bubbled through phosphorus pentoxide in phosphorus trichloride and the oxychloride is removed by distillation.

$$P_2O_5 + 3\,PCl_3 + 3Cl_2 \rightarrow 5\,POCl_3$$

Phosphorus oxychloride is an important intermediate in the manufacture of cyclic and acylic esters for plasticizers, gasoline additives, hydraulic fluids, and organo-phosphorus compounds. It acts as a catalyst as well as a chlorinating agent in several industrial reactions. Other fields of its application are : dopant for semiconductor grade silicon; manufacture of tricresyl phosphate and fire-retarding agents.

Ferric Chloride

Ferric chloride, $FeCl_3$, is a solid composed of dark, hexagonal crystals. Much weak chlorine from chemical processes is reacted with ferrous sulphate or ferrous chloride to get ferric chloride.

Ferric chloride is used for the manufacture of salts, pigments, pharmaceuticals, dyes; as an etching agent for photoengraving; in photography and printed circuitry; as oxidizing, chlorinating and condensing agent; in water purification and waste water and sewage treatment.

TO BE CONTINUED

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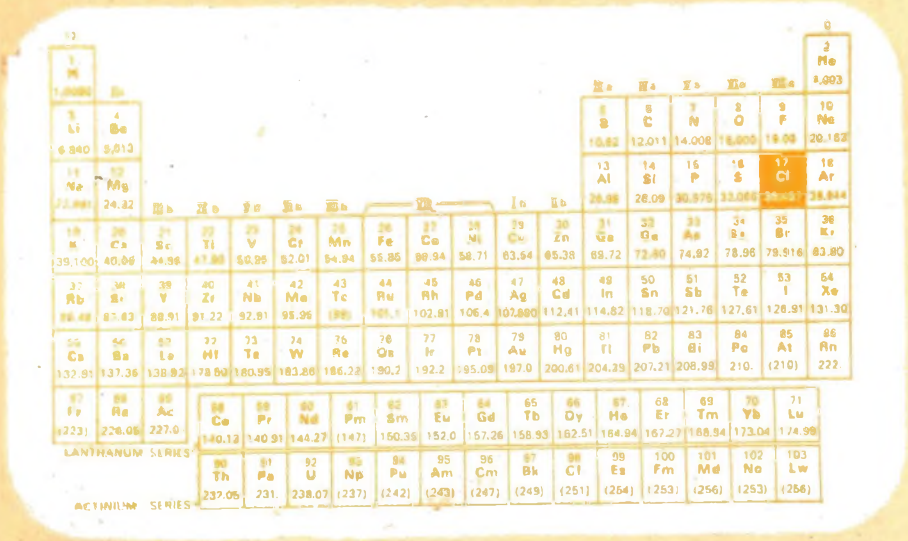
THE STORY OF THE ELEMENTS

Chlorine

(Part III)



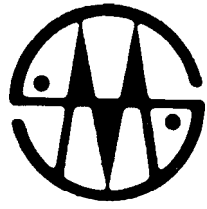
January—February 1979

SARABHAI M CHEMICALS

THE STORY OF THE ELEMENTS

Chlorine

(Part Three)



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CHLORINE

(Part Three)

ORGANIC COMPOUNDS

Chlorine, being the second reactive element, enters into substitution and addition reactions with a number of organic materials to form chloro–derivatives–compounds. Only important ones have been discussed here.

Saturated Aliphatic Compounds

Methane may be chlorinated to a variable extent.

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The reaction may be carried out by light activation or through use of catalysts. It may be controlled to produce methyl chloride mainly, with only slight amounts of other products. Recycling then produces other chloromethanes. If all products are produced in one reaction, they may be separated by distillation.

Methyl Chloride

Methyl chloride, CH_3Cl, is a colourless, non-corrosive, liquefiable gas which condensers to a colourless liquid.

It is made by direct chlorination of methane and a 90% yield can be obtained. It may also be made from methyl alcohol, that to also in 90% yield, by reacting methyl alcohol with hydrochloric acid.

Methyl chloride is used as a catalyst carrier in low-temperature polymerization (butyl rubber). It also finds use in the production of silicones, methyl cellulose, tetramethyl lead, medicines and herbicides. Its miscellaneous uses include : fluid for thermometric and thermostatic equipment; methylating agent in organic synthesis; extractant and low-temperature solvent; and propellant in high-pressure. It is also employed as a refrigerant in cryogenics.

Methylene Chloride

Methylene chloride, CH_2Cl_2 is a clear, colourless, volatile liquid. Direct chlorination of methane is the predominant process and only little is produced by further chlorination of methyl chloride.

Methylene chloride is used in paint removers, as propellant for aerosol sprays, as blowing agent for foams, in solvent extraction, and in solvent degreasing. It is also used in photographic film production.

Chloroform

Chloroform, $CHCl_3$, is a colourless, non-flammable, volatile liquid with characteristic odour and sweet taste. Direct chlorination is the predominant process, although 88% yield may be obtained from the reaction

$$2\ CH_3CO\ CH_3 + 6\ CaOCl_2 \cdot H_2O \longrightarrow 2CHCl_3 + Ca(OAc)_2 + 2\ Ca(OH)_2 + 3\ CaCl_2 + 6H_2O$$

and 80% yield may be obtained by

$$CCl_4 + 2(H) \xrightarrow{(Fe, HCl)} CHCl_3 + HCl$$

Penicilin production requires 42% of the chloroform made, and another 42% is used in the preparation of chlorofluorohydrocarbons, 8% goes into dyes and drugs, and remaining 8% is used as an anesthetic. Minor quantities are used in analytical chemistry, refrigeration, plastics, fumigants and insecticides.

Carbon Tetrachloride

Carbon tetrachloride, CCl_4, is a colourless, non-flammable liquid with sweetish distinctive odour. It yields vapours 5.3 times heavier than air.

Various processes involving chlorination of methane, natural gas or aliphatic hydro-carbons in general yield carbon tetrachloride, but considerable amounts are still produced by the carbon disulphide method which proceeds with 90% yield.

$$CS_2 + 3Cl_2 \xrightarrow{Fe} S_2Cl_2 + CCl_4$$

$$CS_2 + 2S_2Cl_2 \longrightarrow 6S + CCl_4$$

$$6S + 3C \longrightarrow 3CS_2$$

Of the total production, chloroflurohydrocarbons take 70%, grain fumigating 13%, other miscellaneous and chemical uses 12%, fire fighting 4% and industrial cleaning 1%. Its miscellaneous uses include: metal degreasing, agricultural fumigant, chlorinating organic compounds and production of semiconductors.

Ethylene Glycol

The most important product made using chlorine, ethylene glycol, does not contain chlorine itself, but has often been made from the chlorine compound, ethylene chloro-hydrin.

Ethylene glycol, $HOCH_2CH_2OH$, is a clear colourless, syrupy, sweet-tasting, hygroscopic liquid. The chlorohydrin process has been preferred, and

still accounts for about 46% of the production. The chlorohydrin production reaction (70% yield) are :

$$CH_2 = CH_2 + HCl \rightarrow CH_2ClCH_2OH$$

$$CH_2ClCH_2OH + 1/2\ Ca(OH)_2 \rightarrow CH_2{-}CH_2 + 1/2\ CaCl_2 + H_2O$$

(O bridge)

$$CH_2{-}CH_2 + H_2O \rightarrow HOCH_2CH_2OH$$

(O bridge)

Its fields and modes of applications of include : Coolant and antifreeze; asphalt emulsion paints; heat-transfer agent in refrigeration and electron tubes; low pressure laminates; brake fluids; glycol diacetate; polyester fibers and films; low-freezing dynamite; solvent; extractant for various purposes; solvent mixtures for cellulose esters and ethers, especially cellophane; cosmetics (upto 5%); lacquers; alkyd resins; printing inks; wood stains; adhesives; leather dyeing; textile processing; tobacco; and ingredient of deicing fluid for airport runways.

Chloral

Chloral, $CCl_3.CHO$, is colourless, mobile, oily liquid with penetrating odour. Chloral is soluble in water, alcohol, ether and chloroform; and combines with water forming chloral hydrate.

About 50% of chloral production starts with chlorination of ethyl alchol, followed by addition of sulphuric acid and subsequent distillation. The yield is 83%.

$$C_2H_5OH + Cl_2 \rightarrow C_2H_5OCl + HCl$$

$$C_2H_5OCl + C_2H_5OH \rightarrow CH_3CH(OH)OC_2H_5 + HCl$$

$$CH_3CH(OH)OC_2H_5 + 3Cl_2 \rightarrow CCl_3CH(OH)OC_2H_5 + 3HCl$$

$$CCl_3CH(OH)\ C_2H_5 \xrightarrow{H_2SO_4} CCl_3CHO + C_2H_5OH$$

Chlorination of acetaldehyde is the other method of chloral manufacture.

$$2\ CH_3CHO + 3Cl_2 \rightarrow \overset{\text{MIXTURE}}{(CH_2ClCHO + Cl_2CHCHO)} + 3HCl$$

The monochloro- and the dichloro- acetalde mixture is made to react with antimony chloride and excess of chlorine at 80°C to yield chloral in 70% yield.

$$CH_2Cl\ CHO + Cl_2CHCHO + 3Cl_2 \xrightarrow{SbCl_2} 2CCl_3CHO + 3HCl$$

Chloral became important after the world War II with the introduction of newer insecticides. It is mainly used in the manufacture of chloral hydrate and DDT. DDT manufacture consumes 99% of the chloral made.

Other saturated chlorine compounds

Other saturated chlorine compounds of importance are discussed in brief. *Tetrachloroethane,* $Cl_2HCCHCl_2$, is a colourless, heavy, corrosive liquid. It is used as a solvent, in cleansing and degreasing metals; in paint removers, varnishes, lacquers, photographic films, resins and waxes; extraction of oils and fats; alcohol denaturant; organic synthesis; insecticides; weed killer; and fumigant.

Ethylene dichloride, $ClCH_2CH_2Cl$, is a colourless, oily, sweet-testing liquid with a chloroform like odour. Its fields and modes of use include : Vinyl chloride (Wulff process); solvent; lead scavenger in antiknock gasoline; paint, varnish, and finish removers; metal degreasing; soaps and scouring compounds; wetting and penetrating agents; organic synthesis; and ore floatation.

Ethyl chloride, C_2H_5Cl, is a colourless gas than can easily be compressed to a colourless, flammable liquid. It is mainly used in the manufacture of tetraethyl lead and ethyl cellulose. Other applications include : as an anesthetic; and alkylating agent in Organic synthesis; in refrigeration; as a reagent in analytical chemistry; solvent for sulphur, phosphorus, fats, oils, resins and waxes; and in insecticides.

Ethylidene chloride, CH_3CHCl_2, is a colourless, neutral, mobile liquid,

having an aromatic ethereal odour, with saccharin taste, It is used in medicine, as an extraction solvent and in fumigants.

Pentachloroethane, $CHCl_2CCl_3$, is a dense, high-boiling, colourless liquid. It finds use as a solvent for oil and grease in metal cleaning. Also used for separation of coal from impurities by density difference.

Hexachloroethane, Cl_3CCCl_3, is a colourless, crystalline compound possessing a camphor-like odour. Its various fields of application are : Organic synthesis; retarding agent in fermentation; camphor substitute in nitrocellulose; rubber accelerator; pyrotechnics and smoke devices; solvent and explosives.

Propylene chloride, $CH_3CHCl\ CH_2Cl$, is a colourless, stable liquid with chloroform-like odour. Its varied applications include : intermediate for perchloroethylene and carbon tetrachloride; lead scavenger for antiknock fluids; solvents for fats, oils, waxes, gums, and resins; solvent mixtures for cellulose esters and ethers; scouring compounds; spotting agents; metal degreasing agents; and soil fumigant for nematodes.

1:2:3 – Trichloropropane, $CH_2Cl\ CHCl\ CH_2Cl$, is a colourless liquid. Good solvent for oils, fats, waxes, chlorinated rubber and numerous resins. Also used as a paint and varnish remover and a degreasing agent.

n-Butyl chloride, $CH_3CH_2CH_2CH_2Cl$, is a colourless liquid. It is used as an alkylating agent in organic synthesis; as a solvent and in the medicine.

1:4 – Dichlorobutane, $ClCH_2(CH_2)_2CH_2Cl$, is a colourless, mobile liquid, with pleasant odour, and is used in the organic synthesis, particularly adiponitrile and nylon.

Amyl chlorides, $C_5H_{11}Cl$, are straw to purple coloured liquid, used as chemical intermediates, in the manufacture of other amyl compounds; as a solvent; as rotogravure ink vehicle and in soil fumigation.

Dichloropentane, $C_6H_{10}Cl_2$, is a mixture of dichloro derivative of both normal-and iso-pentane. About 40% are amylene di-chlorides having two chlorine atoms attached to adjacent carbon atoms. It is a light yellow coloured liquid. When pure, it is used as a solvent in the oil, grease, rubber, resin, and paint industries. It is also employed in other fields, such as : removal of tar; reclaiming of rubber: paint and varnish removers

degreasing of metals; insecticides, soil fumigant and removal of wax deposits on a oil-well equipment.

Chlorinated paraffins are paraffin oil or wax in which some of the hydrogen atoms have been replaced by chlorine. They are used as plasticizer for polyvinyl chloride in polyethylene sealants; as flame retardant in plastics and textiles; in detergents; as lubricant additives; in high pressure lubricants; and as weather-proofing agents.

Unsaturated Aliphatic Compounds

Perchloroethylene

Perchloroethylene, $Cl_2C = CCl_2$, is a colourless, nonflammable, stable heavy, toxic liquid. It is miscible with alcohol, ether, and oils, but is insoluble in water.

It is made by two process : (a) by chlorination of hydrocarbons, and pyrolysis of the carbon tetrachloride also formed; (b) from acetylene and chlorine via trichloroethylene.

It is used as a dry-cleaning solvent; as a vapour degreasing solvent; as a drying agent for metals and certain solids; in vermifuge; as a heat-transfer medium and in the manufacture of fluoro-carbons.

Trichloroethylene

Trichloroethylene, $CHCl : CCl_2$, is a stable, low boiling, colourless. non-flammable, heavy, toxic, photo-reactive liquid, having chloroform-like odour. It is miscible with common organic solvents and slightly soluble in water.

It is prepared from tetrachloroethylene by treatment with lime or alkali in the presence of water, or by thermal decomposition, followed by steam distillation.

The various fields of applications of trichloro-ethylene are : metal degreasing; extraction solvent for oils, fats and waxes; solvent dyeing; dry cleaning; refrigerant and heat exchange liquid; fumigant; cleaning and drying electronic parts; diluent in paints and adhesives; textile processing chemical intermediate; and aerospace operations (flushing liquid oxygen).

Allyl Chloride

Allyl chloride, $CH_2 = CHCH_2Cl$, is a colourless liquid with unpleasant pungent odour. It is miscible with alcohol, chloroform, ether and naphtha, and insoluble in water.

It is made by high-temperature chlorination of propylene from petroleum cracking, at 15 psi and 400–500°C. The product is purified by distillation. It is used in the preparation of allyl alcohol and other allyl derivatives; in preparing thermosetting resins for varnishes, plastics, and adhesives; in the synthesis of pharmaceuticals and insecticides; and in the manufacture of glycerol and epichlorhydrin.

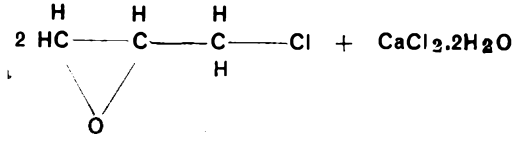
Epichlorhydrin

Allyl chloride is made to react with hypochlorous acid to make dichlorohydrins

$$CH_2 = CHCH_2Cl + HOCl \longrightarrow CH_2OHCHClCH_2Cl$$

which may in turn be reacted with lime to produce epichlorohydrin.

$$2\ CH_2OH\ CHCl\ CH_2Cl + Ca(OH)_2 \rightarrow$$

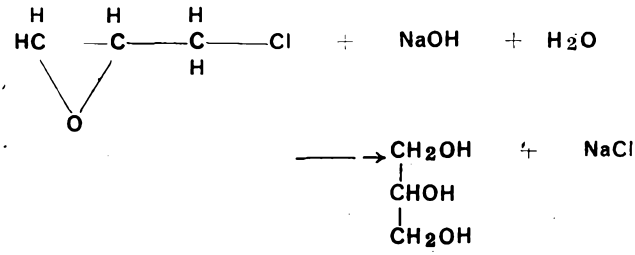


$$+ CaCl_2.2H_2O$$

Epichlorhydrin is the major raw material for epoxy and phenoxy resins; in the manufacture of glycerol; for curing propylene-based rubbers; as a solvent for cellulose esters and ethers; and in the preparation of high wet-strength resins for paper industry.

Glycerol

Epichlorhydrin is finally hydroclyzed to form glycerol with sodium hydroxide in 75–80% yield.



Glycerol is a clear, colourless, odourless, hygroscopic, syrupy liquid with sweet taste. Its fields of applications are so wide that only important ones are listed here : alkyd resins; explosives; ester gums; pharmaceuticals; perfumery; plasticizer for regenerated cellulose; cosmetics; foodstuffs, conditioning tobacco; liqueurs; solvent; printer's ink rolls; polyurethane polyols; emulsifying agent; rubber stamp and copying inks; binder for cements and mixes; paper coating and finishes; special soaps; lubricant and softener; bacteriostat; penetrant; hydraulic fluid and humectant.

Vinylidene Chloride

Vinylidene chloride, $CH_2 = CCl_2$, is a colourless, low-boiling liquid made by the reaction of acetylene with chlorine in the presence of tetrachloroethane and ferric chloride at 135°C, by treating 1: 1: 2-trichloroethylene with alkali. It polymerizes easily and hence is used to make co-polymers, such as saran, Geon, and Velon.

Vinyl Chloride

Vinyl chloride, $CH_2 = CHCl$, is a colourless gas made by the reaction of acetylene and hydrochloric acid, using catalysts such as mercury salts, or by treating ethylene chloride with alkali, It polymerizes to make polymers such as Koroseal, Vinylite, Geon, Tygon, Velon, and Saran.

Other Miscellaneous Unsaturated Compounds

Beside the important unsaturated compounds listed above, there are a few such compounds which also require a passing reference to them.

Chloroacetylene, $HC \equiv CCl$, is an unstable gas; whereas *Dichloroacetylene,* $CCl \equiv CCl$, is a colourless gas which is quite explosive; and *Methallyl*

chloride, $CH_2 = C(CH_3)\ CH_2Cl$, is a colourless to straw-coloured volatile liquid with a sharp, penetrating odour. It has been employed as an intermediate for the production of insecticides, plastics, pharmaceuticals and other chemicals; and also as a fumigant for grains, tobacco and soil. *Chloroprene* $H_2C = CHCCl = CH_2$, is yet another compound of interest. It is a colourless liquid, soluble in alcohol and slightly soluble in water. It is mainly used in the manufacture of neoprene, synthetic rubbers and plastics.

Alicyclic Compounds

Benzene Hexachloride

Benzene hexachloride, $C_6H_6Cl_6$, forms colourless to yellow crystals or flakes. It is a mixture of isomers of 1: 2: 3: 4: 5: 6–hexachlorocyclohexane.

Direct chlorination of benzene, using the light from a mercury vapour lamp to activate the reaction, produces a 95% yield of a mixture of geometric isomers.

$$C_6H_6 + 3\ Cl_2 \xrightarrow{\text{light}} C_6H_6Cl_6$$

The γ–isomer is toxic to insects and is concentrated by crystallization, steam distillation and further fractional cyrstallization. Its use is restricted as an insecticide only.

Lindane is the legal label name given to the gamma – 1: 2: 3: 4: 5: 6–hexachlorocyclohexane.

Chlordan

Chlordan or chlordane, $C_{10}H_6Cl_8$, is a colourless, odourless, viscous liquid. It is soluble in many organic solvents, insoluble in water; miscible in deodourized kerosine and decomposes in weak alkalies. It is used as an insecticide in the form of oil emulsions, dusts and dispersible liquids.

Aromatic Compounds

Chlorobenzene

Chlorobenzene, C_6H_5Cl, is a colourless, mobile, volatile liquid with an

almondlike odour. It is miscible with most organic solvents and insoluble in water.

Chlorination of dry benzene at 40°C using ferric chloride or other catalyst in iron tanks produces mono-chlorobenzene at 70-75% yield.

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

Phenol production consumes 60% of the total production of chlorobenzene, 25% goes into the DDT manufacture, whereas the remaining 15% is consumed by aniline and allied products. Besides these, it is also used as a solvent carrier for methylene diisocyanate and as a pesticide intermediate.

Dichlorobenzene

Dichlorobenzene, $C_6H_4Cl_2$ exists in two isomeric forms. The *Ortho-* form is a colourless, volatile liquid, whereas the *para-* isomer consists of white volatile crystals. It is obtained by chlorination of monochlorobenzene.

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$

Mixtures of *mono-* and *di*-chlorobenzene may be made slightly alkaline, allowed to settle, and then separated by fractional crystallization. The *para* form usually is present in three times the amount of the *ortho* isomer. Small amounts of polychlorobenzenes are also simultaneously produced.

para-Dichlorobenzene is consumed in moth repellents, general insecticides, germicides and space odourants. It is also used in the manufacture of 2:5-dichloroaniline, dyes, intermediates and pharmaceuticals. It is used in agriculture in fumigating soil.

The applications of *Ortho*-dichloro benzene include : manufacture of 3:4-dichloroaniline; solvent for a wide range of organic materials and for oxides of non ferrous metals; solvent carrier in production of toluene diisocyanate; manufacture of dyes fumigants and insecticides; degreasing hides and wood; metal polishes and industrial odour control.

Other Aromatic Compounds

Benzyl chloride, Benzal chloride and Benzotrichloride with formulas $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$ and $C_6H_5CCl_3$, respectively, are colourless liquids. They are used as starting materials for the synthesis of pharmaceuticals

(Benzedrine, Demerol). They are also employed as constituents of perfumes, and as starting materials for the preparation of insecticides and insect repellents. They also find use as lubricants and as intermediates in dye manufacture.

The *Chlorinated biphenyls* find use in electrical insulation, hydraulic mediums, lubricants, and as constituents of paints varnishes, and plastics. They are chemically inert. *Chlorinated naphthalenes* are used in chemical, lubricant, and electrical insulation applications.

Pentachlorophenol, C_6Cl_5OH, is a white crystalline powder, made by the chlorination of phenol.

$$C_6H_5OH + 5\ Cl_2 \rightarrow C_6Cl_5OH + 5\ HCl$$

It is mainly employed as a wood preservative. It is also used as a fungicide, bactericide, algicide, and herbicide.

Dichlorophenol, $Cl_2C_6H_3OH$, is a white, low melting solid, and is also made by chlorination of phenol. It is used in the organic synthesis in preparation of other chlorine compound 2:4-dichlorophenoxy acetic acid, most popularly known as 2:4-D. 2:4-D is widely used as a weed-killer.

Miscellaneous Compounds

Phosgene

Phosgene, $COCl_2$, is a colourless to light yellow coloured, poisonous gas having strong stifling odour in concentrated form and hay-like odour in dilute form. It is derived by passing a mixture of carbon monoxide and chlorine over activated carbon. It is used in Organic synthesis, especially in the manufacture of toluene isocyanate and other isodyanates polyurethanes and polycarbonateresins, carbamates, organic carbonates and chloro formates; pesticides; herbicides and dye manufacture. Toluene diisocyanate is, in turn, becoming important in making foams and special rubbers. Other Isocyanates are being used in making adhesives.

Monochloroacetic acid

Monochloroacetic acid $CH_2ClCOOH$, is a colourless to light-brownish crystaline substance. It is derived by the action of chlorine on acetic acid in the presence of acetic anhydride, phosphorus or sulphur, in acid-

resistant equipment. It is used as a chemical intermediate for making dyes, coumarin, pharmaceuticals, cosmetics weed-killers, and insecticides.

Dichloroacetic acid

Dichloroacetic acid, $CHCl_2COOH$, is a colourless liquid resulting from the further chlorination of acetic acid. It is used as an intermediate in chemical manufacture.

Trichloroacetic acid

Trichloroacetic acid, CCl_3COOH, is a deliquescent colourless, crystalline substance with very sharp, pungent odour. It is made by still further chlorination of acetic acid. It is used medicinally, and the sodium salt is used as a weed-killer.

Other compounds such as *Chloramines* have been promoted as bactericides, germicides, and surgical antiseptice.

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